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STUDY OF AMMONIUM NITRATE MATERIALS

Arthur D. Little, Incorporated

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STUDY OF AMMONIUM NITRATE MATERIALS

Progress Report No. 11

This report covers the period from May 1 to September 15, 1952, and is concerned with large scale experiments o' scaled experiments which attempt to demonstrate the general theory of the fire and detonation in the several ship disasters of ammonium nitrate.

Large Scale Experiments

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By R. M. Hainer

R. M. Hainer

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CONSIDERATION OF LARGE SCALE AND MODEL EXPERIMENTS AT ELEVATED TEMPERATURES

I. INTRODUCTION

The objective of this research on ammonium nitrate from the beginning has been to develop a comprehensive theory which is a synthesis of all the information available on the behavior of this material. The purpose of the building of such a theory is to lead to experimentation that either extends or confirms our knowledge. While in some measure the work that has been reported has demonstrated the validity of this approach, a further aim has been suggested, both by members of the Advisory Committee and by the logic of the problem. This aim is the preparation and accomplishment of a moderately large scale demonstration of the danger and violence of ammonium nitrate which on the face of the evidence would be similar to the great disasters and would be convincing of the correctness of the formulation concerning ammonium nitrate. Considerable thought has been given to this aim by many researchers prior to the initiation of this project. No one has fully accomplished this purpose. The series of tests at the A. P. Hill reservation were directed to this goal; the large bomb tests at Picatinny Arsenal, as nearly as any tests, have demonstrated the violence of ammonium nitrate under conditions of confined burning. The questions which were not answered in these tests were: Is not the confinement in pressure during a fire that leads to detonation within a sealed high-explosive shell casing greater than could be reasonably expected in a ship fire? —and does detonation occur with only the moderate confinement in pressure that can be present in a ship's hold?

Purpose: The purpose of the large scale test has been to achieve an obviously convincing demonstration of either of two results: (1) the development of a fire as a result of spontaneous heating or, the opposite, the demonstration that spontaneous heating does not occur, or (2) the development of an explosion (either deflagration or detonation) that is initiated from a fire alone.

In formulating the purposes of a large scale demonstration under the present contract, the requirements of the United States Coast Guard are paramount. The Coast Guard requires rules of shipment which provide for safety in transit. Our purpose, therefore, is to define conditions under which spontaneous heating does not cause fire and where fire, no matter what the cause, does not lead to explosion. We have tried to determine the conditions for safe handling of ammonium nitrate by demonstrating the conditions under which a spontaneous fire begins and an explosion occurs, but due to the inherent difficulties which are herein fully enumerated, only a partial realization was obtained.

Difficulties of all large scale experiments: First, any experiment which is undertaken but once or twice must involve only exceedingly probable or reproducible mechanisms. The development of a fire and explosion in a cargo in only one in ten or one in 100 ostensibly similar circumstances is a risk which must be avoided, and yet experimentation which reproduces the initial circumstances with the same probability for the result is a complete failure, and the checking of the results of other workers is impossible.

Second, experimentation with any considerable amount of ammonium nitrate involves a hazard because of its fire and potential explosion danger. Even the seemingly trivial amounts of several hundred pounds involve considerable precautions if detonation is possible and yet a few pounds can lead to unusual fire.

Throughout this research these two primary difficulties have plagued experimentation. At this juncture, even though the main lines of evidence have been drawn, much is yet desired to fully understand the behavior of ammonium nitrate.

Size of the experiment involving fire and explosion: As has been indicated above, the two main problems in the behavior of ammonium nitrate are the nature and development of spontaneous heating and the nature and development of deflagration and detonation.

In either case, ample evidence has been presented that the quantity of ammonium nitrate involved in a cargo, that is, the size of the pile, is an important determinant of the result of heating or fire. Progress Report 8 defines the radius for self-heating in terms of the absolute temperature, thermal conductivity, activation energy for reaction, heat of reaction, and rate of chemical reaction and by this relationship establishes a "critical radius" below which heating cannot occur under given conditions.

Progress Report 9 amplifies the previous data and shows that the pressure developed in a fire is related to the progress of deflagration and detonation. The pressure developed by "hot spot" fires is related to the size of the pile of ammonium nitrate.

From this it is clear that an adequate representation of a ship fire is not obtained in a scaled model where "effective radius" or "pressure drop" is involved in the scaling.

II. CONSIDERATION OF LARGE SCALE EXPERIMENTS CONCERNED WITH SPONTANEOUS HEATING

The necessary and sufficient conditions for spontaneous heating are: (1) that heat is generated and (2) that the heat generated does not entirely escape from the mass of material. Obviously, the effect of self-heating will be at a maximum when all the heat generated is unable to escape. The thermal conductivity or the diffusivity can be used to measure the escape of heat in a solid pile. This conductivity has been measured and is very small in ammonium nitrate, so that a large pile of ammonium nitrate is very effectively insulated by the nitrate itself. The rate of development of heat is most strongly dependent on the rate of reaction which is itself an exponential function of the absolute temperature. Since there are no reasonable grounds and no testimony in favor of measurable spontaneous heating for wax coated FGAN in paper bags at room temperature (mixed fertilizers with peanut hulls, etc., may perhaps be spontaneously heating from 30°C), the material must be, initially, at an elevated temperature to carry out experimentation. Since the uniform heating of a large pile of nitrate is impractical experimentally, it being technically difficult and dangerous in both the heating and the knowledge of how heating is progressing, such experimentation must take place near the manufacturing operation where high-pan and graining kettle operations are carried out. In order that a reasonable pile be involved, at least some 10 to 20 tons of hot nitrate are required to be assembled without loss of temperature in assembling, to be instrumented without providing heat leaks, and to be isolated sufficiently to allow for a sizable fire and possibly for an explosion.

Two possible producers of waxed FGAN were interviewed to try to arrange for a spontaneous heating experiment; they were Hercules Powder Company and Atlas Powder Company, both of Wilmington, Delaware. Both were direct and positive in their refusal to allow such work for several reasons, as for example not having adequate isolated property close enough for ready transfer of the hot nitrate and not wishing to be in any way involved publicity if a fire should result. Both manufacturers were quite willing to cooperate in supplying nitrate waxed to specification. The former manufacturer has supplied, at cost, four tons for research to Dr. McKenna of the Bureau of Explosives and to Arthur D. Little, Inc.

As can be seen from Table I of Progress Report 10, a spherical pile of approximately 13 tons and 10 feet in diameter initially at a given elevated temperature would require 8.8 days for the cooling wave to penetrate from the outside edge to the center, in the absence of the generation of heat. With heat generation present, a temperature is possible for this size pile for which the center would remain at the given initial temperature indefinitely. Practically speaking, as long a time as three times 8.8, or 26 days might be required to determine that cooling is assured. Should cooling be affirmed, no evidence is forthcoming from the same experiment as to what initial temperature would be necessary to assure a continued temperature rise which, if not interrupted, would lead in time to an internal fire. Once cooling has begun through the pile, reheating to a new initial temperature is not possible by any known means, e.g., wires for heating a pile would be the primary source of heat leak from the pile.

Therefore, (1) because of an inadequate supply of heated nitrate, or a method of heating or reheating nitrate, (2) because of no suitable place near the manufacturing operation which could allow the experiment, (3) because of the long time required to

observe the results, (4) because of the meager information obtained from any one experiment, and (5) because of the difficulty of proper instrumentation, the attempt to carry out a large scale spontaneous heating experiment to demonstrate dramatically the behavior of ammonium nitrate has been abandoned.

III. SCALED EXPERIMENTS CONCERNING SPONTANEOUS HEATING

Since a large scale spontaneous heating experiment is not possible, it would be very desirable to confirm experimentally the formulation of the theory of spontaneous heating given in Progress Report 8 for intermediate size samples of ammonium nitrate. Such confirmation on intermediate sized samples would establish experimentally the constant, δ of the Frank-Kamenetsky theory, since all other parameters are based on experimental observations. This desirable confirmation of the theory would allow extension of the results to ship-sized cargoes and full appreciation of the limiting temperatures which can lead to a fire.

In principle, a 10 to 20 liter flask filled with ammonium nitrate heated slowly to achieve a uniform control temperature and insulated in an inert insulator such as "Santocel" Grade A (a Monsanto silicon gel product manufactured at Everett, Mass.) could provide the desirable experimental confirmation for a sample equivalent to a very large size pile. However, in practise, the limiting conditions have not been accomplished: (1) because of the difficulty of obtaining an AN sample which was uniformly and quickly heated to a temperature where self-heating is rapid, or (2) because of the difficulty of obtaining adequate and adjustable isolation for a sample of nitrate so that a moderate sample is equivalent to a much larger size sample, (3) finally, because of the difficulties associated with the experiments in which losses are electrically compensated by a heated baffle whose temperature

is maintained slightly less than that of the sample. For the latter, statements concerning the adequacy of the precision of compensation often remain unconvincing.

Spontaneous Heating Experiments:

1. A preliminary self-heating experiment with 4.5 kg of FGAN (Texas City) reported in Progress Report 1C showed defect (1 above), and ignition occurred in the region of 170-180°C.

2. A sample of 5.3 kg of (Texas City) FGAN was heated in a five-liter flask with a surface heater on the flask and buried in Santocel in a 55 cm diameter 90 cm high fiber drum, the minimum distance from flask to barrel in Santocel being 16 cm. After the outside of the flask was held six hours slightly above 150°C and the inside was eleven hours close to but above 130°C, the thermocouples corroded. The sample was set off by electrical heating to observe closely the intensity of the fire. Fire developed at a temperature near and perhaps slightly above the melting point, and gas phase temperatures over 500°C (limit of recording chart) were quickly developed and maintained for about 40 minutes. The reaction was not rapid, the nitrate burned by flames working through the sample without the accumulation of liquid. The clay filler was left in a friable but still a honeycomb structure indicating only moderate burning rates. All of the sample was consumed, and the heating coil on the flask was destroyed. The progress of the fire could be inspected at close range, and limiting the escape of the product gases produced rapid-flow whistling. The gaseous products were ruby red, indicating NO_2 in large quantities. White fumes were for the most part absent.

3. A sample of 5.4 kg of Hercules 0.8 per cent paraffin coated FGAN was similarly heated and insulated in Santocel. Shredded bagging paper was added to about 0.8 per cent. Shredding is allowable to represent the maximum hazard approached for broken bagging in a cargo near corners of several bags. This sample fumed off after 16 hours at 150°C and two hours from 160 - 165°C; the maximum recorded temperature prior to rapid self-heating was 165°C. The pyrex flask became softened in the fire which again left a friable honeycombed residue of clay. All of the sample was consumed.

4. A sample of 4.4 kg of ammonium nitrate fertilizer Aeroprills (American Cyanamid Company, New York, made in Canada), which is clay coated without wax, was heated in a five-liter flask equipped with a 150°C limit switch at a slow heating rate.

Heating took place as before in a fiber barrel filled with Santocel. In three days, evidence of gas evolution was present at a temperature near 150°C. In five days the sample was giving off acid gases and was found to be molten at 180°C, having self-heated from 150°C. The sample by analysis was 0.3 per cent acid. The product gases were analyzed and found to contain mainly N_2O but some CO_2 and a trace of NO_2. The CO_2 presumably came from organic material in the clay.

Measurement of the rates of decomposition gave fractional rates of 0.14×10^{-6} moles per second at 145°C and 5.1×10^{-6} moles per second at 187°C. Self-heating raised the temperature about 12°C in 2-1/2 hours at 185°C. The rate of decomposition and, therefore, self-heating, was about 100 times greater than that for CPAN. Temperature control was achieved by adding additional cold sample. The by-then 6.4 kg sample was removed to the country during which process freezing occurred. After two days, a temperature of 180°C was again obtained still with the 150 $\pm$ 5° Centigrade

temperature switch in operation. Self-heating occurred, as was recorded, and after remelting with the heater disconnected, self-heating raised the temperature slowly to 220°C where the cork stopper in aluminum foil became eaten away, and an opening occurred letting in air from the outside. This event allowed cooling by convection and the sample cooled to below the freezing point. The acid content after freezing was 0.15 per cent HNO_3 instead of the 0.3 per cent found earlier.

The importance of this experiment is twofold: (1) samples of technical grade, wax-free, clay-containing, fertilizer-grade, prilled ammonium nitrate can go acid on heating and, if acid, the rate of decomposition and, therefore, the spontaneous heating is sufficient to produce observable self-heating in the range of 150°C. (2) The self-heating to the range of 200°C did not produce rapid, local, further self-heating to the flame point as with wax-coated FGAN, although the result given was achieved without paper in the nitrate.

5. A sample of 5.3 kg of Hercules 0.8 per cent paraffin coated ammonium nitrate was heated in a five-liter flask with an external heater on the surface of the flask and with the temperature limited by a 125 ± 5°C switch inside a barrel of Santocel as before. The heating was continued for approximately 28 days with an inside temperature of about 130°C. The maximum daily inside temperatures are as follows: July 23 - 130 ± 1°C, 24 - 133, 25 - 132, 26 - 132, 27 - 133, 28 - 132, 29 - 133, 30 - 133, 31 - 132, August 1 - 133, 2 - 132, 3 - 133, 4 - 133, 5 - 133, 6 - 136, 7 - 138, 8 - 140, 9 - 141, 10 - 145, 11 - 145, 12 - 146, 13 - 147, 14 - 149, 15 - 154. The outside flask temperatures range from 110 to 115°C (thermocouple may not have been in good contact with the flask) and for the last several days rose to 123°C giving about 30°C less than

inside temperature. Maximum daily temperatures were used because of slight drifting of about 5°C as the result of the phase lag in the heating and cooling of the temperature compensating thermal junction, compared with the ambient temperature. Corrosion prevented the continuation of the heating.

The sample was 80 per cent very dark brown sintered FGAN which showed considerable scorching of the paraffin. A small fraction of the FGAN sample on the bottom of the flask showed wax migration and an increase in density. While care was taken to obtain uniformity in the heater construction, there was evidence that some heating variation occurred in the sample which was not recorded on the two thermocouples.

We conclude that a sample of FGAN has shown self-heating at approximately 130 - 135°C, although for the apparatus used, a long delay is required before ignition takes place. The difference of the added wax in FGAN compared to Aeroprills is twofold: to enhance low temperature reactions without acid and to carry the reaction to the ignition of a flame.

6. A sample of 9 kg of Hercules FGAN coated with 0.8 per cent wax "B" (same as in Texas City FGAN) and 0.80 kg of torn up bagging paper was heated in a ten-liter flask on a hot plate in a barrel of Santocel. The flask was not wire wound as before, because a more rapid, less expensive, and less corrosion susceptible apparatus was desired. Because Santocel has been criticized as a poor radiation insulator (at temperatures below 100 to 150°C the criterion is not valid), the flask was wrapped with glass wool and aluminum foil and then set in Santocel on a non-radiant hot plate equipped with a 120 $\pm$ 5°C limit switch. The heat losses from the sample were so large that only temperatures of 50° to 70°C were

recorde.. After 11 days, the set-up was changed and the flask was set inside a 16 quart aluminum cooking kettle, the limit switch being attached to the kettle wall. Eighty minutes after this change, as a result of a thermal phase lag to the limit switch with an inside temperature of 72°C and with the outside temperature at 180°C, self-heating occurred, and the resulting fire destroyed the insulating barrel. This experiment had both difficulties (1) and (2) above. While again a precise experiment was not achieved, the conclusion that at or below 180°C, spontaneous heating to flame and 500°C gas temperatures is inescapable. A similar experiment has been reestablished with the limit switch on the hot plate instead of on the cooking kettle; the limiting temperature currently is of the order of 100°C. Further progress will be reported at a later date.

7. A sample of 10.5 kg of Hercules EGAN coated .23 kg C.P. sodium chloride (2.2 per cent) and .23 kg bagging paper (2.2 per cent) with 0.8 per cent paraffin were heated in a ten liter flat bottom flask on a hot plate, the temperature of which was limited by a 120°C thermal switch. The flask was wrapped with glass wool and aluminum foil, but the temperature in the flask did not attain temperatures above 50°C to 70°C during 21 days of heating. The apparatus was then rebuilt into a 16-quart aluminum kettle with the temperature limit switch on the hot plate. In the subsequent 22 days the recorded temperature remained at the order of 100°C without noticeable activity. The experiment continues.

8. A 100 pound paper covered bag of du Pont C.P. ammonium nitrate was wound on the paper surface with resistance wire and inserted in a sealed fiber barrel surrounded by Santocel; a connection was made to observe the gas evolution during heating. The temperature reached 110 - 120°C on May 25, 1952; by June 6,

the center temperature was stabilized at a maximum of 134°C. This temperature was maintained by the operation of a limiting switch set for 130°C and an almost continuous current of 34 watts until June 16, a total of 22 days above 110°C. During this time, gas was given off at a rate of 200 to 250 cc per hour. Since the free volume of the barrel was large, the gas flow was not regular, but changed and even reversed, with the changing temperature of the surroundings; the average value was, however, maintained. Infrared analysis of the product gases showed CO_2 and N_2O; in the ratio of 0.7 to 1. On June 16, corrosion at the electrical junctions dropped out a section of the heating coil, and an approximate wattage readjustment was made to maintain the temperature of the sample. The temperature limit switch remained operative on a heated portion of the sample. The adjustment, while considerably below the full wattage, was erroneously high, and approximately 24 hours later, in spite of the limit switch, the sample caught fire, breaking open the fiber barrel, filling the laboratory with NO_2 and scattering Santocel. Water extinguished the fire which burned some ten minutes. Examination of the remaining mass showed: (1) that the fire had burned largely in cigarette type burning on parts of the surface of the sample only; (2) that all the paper bag had disintegrated prior to the fire, leaving an outer edge of darkened, softened, reactive, ammonium nitrate-cellulose residue; (3) that a local section had heated to a temperature perhaps as high as 170°C, although only traces of molten nitrate were found after the fire. Approximately 1/5 of the sample was lost in the fire. The surface of the ammonium nitrate which was blackened by paper was found to be 0.09 to 0.19 per cent acid (as HNO_3) on the following day. The mushy nitrate was 0.06 - .07 per cent acid; the fused crystals were 0.03 per cent acid, and the central mass which was the major portion of this caked CPAN was unchanged showing 0.00 per cent acid. Tests for nitrite and nitrocellulose proved negative.

The thermal limit switch, the current limiting fuses, the variacs were all operative after the experiment, indicating no major apparatus failure. However, it is obvious that self-heating had taken place from the region of the melting point, and that this self-heating had been in acidic cellulose-ammonium nitrate residues that had been formed on the three weeks' heating at 134°C. Chemically pure nitrate does not of itself self-heat to flame and NO_2 products, and of itself does not self-heat appreciably until of the order of 50°C above the melting point (this temperature is not accurately known for a radius of one bag). The experiment serves as a reminder that self-heating is a function of the conditions of the sample and that the worst conditions are not found by experiments of short duration on fresh samples of nitrate. Acidity is extremely important. The kinetics of decomposition show reactivity from 100 to 500 times that for pure nitrate alone and greater than for FGAN without paper or acid. Such a fire of FGAN would not have been so easily extinguished, however, because of the additional exothermic contribution of the wax coating.

9. Recently, 1.6 pounds of FGAN coated with wax "B", with 2.5 per cent added paper, and 0.7 per cent added water was heated by a surface heater on a one-liter flask equipped with a temperature limiting switch. This flask was placed inside of a wide mouth, large size Dewar which was heated on its outside surface and on a cover plate to eliminate heat losses by externally controlled heaters. The flask was wrapped in glass wool in the Dewar which was itself wrapped in glass wool and inserted in Santocel in a barrel. The apparatus was stabilized at 132 ± 2°C for four days and without a change in the adjustments the above-mentioned FGAN was added; after 35 hours, fire developed, and the sample burned off. The apparatus was observed by periodic, non-continuous temperature measurements on four thermocouples.

We conclude that when care is taken to eliminate heat losses, self-heating to fume-off is possible with FGAN, paper and moisture from 132°C in as little as 35 hours.

IV. FIRE IN AMMONIUM NITRATE

A sample of 100 pounds of Hercules FGAN coated with 0.8 per cent wax "B" was set on fire by approximately one pound of thermite buried in the upper one-third of the bag of nitrate. After the initial flaming of the thermite, the reaction proceeded with vigor, but burning continued largely without the collection of liquid. The material burned by hot zones working through the material. The rate of burning was controlled largely by the burning surface instead of the temperature of the nitrate, since the nitrate was essentially cool until invaded by the hot zone; the thickness of the liquid zone is of the order of a few millimeters or less. The fire could be extinguished only if the material could be broken apart and the fire exposed to spreading action by shoveling.

This experiment was repeated by placing about one pound of charcoal brickets beneath the thermite in a layer across the bag of Hercules FGAN coated by 0.8 per cent wax "B". The action of the fire in this experiment was noticeably different. After the reaction of the thermite, the nitrate began to burn by the migration of hot zones through the material as before, but soon the charcoal became ignited, and the vigorousness of fire increased. The center of the charcoal brickets burned at red heat in the products of ammonium nitrate sublimation and decomposition; the dissipation of the greater exothermy of the charcoal in hot product gases melted considerable amounts of nitrate not found to as great an extent in the absence of

carbon. The melting nitrate in contact with the charcoal quenched the surface and carried away carbon, giving the liquid a black tar-like appearance. The hot liquid from the center of this bag subsequently began to splash its way out, forming a kind of boiling "mud pot." Liquid was splashed several feet from the bag. This action became still more vigorous within a minute or two, and the collected liquid self-heated to the temperature limiting point and fumed off, throwing burning nitrate over a circle of five to ten feet in diameter. During this brief fume-off phase the fire could not be approached.

This fuming-off could happen several times in succession by providing sufficient fuel and by holding the liquid within the nitrate bag. The rate of reaction in this experiment was enhanced over the previous experiment where fire was present without the collection of liquid (1) by the temperature and rate of decomposition of the accumulated hot liquid, and (2) by the added fuel charcoal. The fire could be extinguished by vigorous shoveling and spreading, except during a fume-off period.

Obviously, in either experiment the fire could not be extinguished by burying in earth, although by sufficient cover all the gases and white fumes were filtered out so that the location of the fire was not apparent. Subsequently, however, a vent or chimney developed through even a number of inches of covering sand.

It is believed that the fume-off of the liquid, in contrast to the hot zone or propellant burning alone, is a very important aspect of the ship fire, the pressure development, and the eventual development of detonation.

Recently a somewhat larger fire was set in wax "B" coated FGAN. A 55-gallon steel drum set in a hollow 5 feet deep by 20 feet across was loaded with 300 pounds of FGAN intermingled with five pounds of charcoal and perhaps 30 pounds of wood. This mixture was ignited by one-half pound of thermite starter and 22 pounds of thermite. After an initial flaring to from 10 to 15 feet of white flame, a fire of rapid intensity developed. No white fumes or brown fumes were visible as long as the intensity of the fire was retained. Forceful splattering of liquid AN developed at the holes made in the barrel by the thermite. Care was taken in approaching the fire for fear of rapid fume-off; such fume-offs did not occur primarily because the heat did not allow marked accumulation of liquid AN from the initially cold material. The intense heat assured rapid burning to any portion of the sample which became exposed. One hundred pounds of similar FGAN was added during the fire in two sections. Considerable flaring of the fire took place; no unusual pressure appeared to develop in the degree of confinement of a barrel.

One hundred pounds of Aeroprills clay-coated AN were added to the attenuated FGAN fire with similar flaring and burning. "Mud pots" of molten splattering AN developed at the base outside and under the barrel. The addition of thermite to these zones produced fierce blasts of white heat from below the liquid surfaces and from under the barrel, indicating minor pressure development, but no explosions developed.

The addition of 150 pounds of Forbwerke Hoechst 60 per cent ammonium nitrate 40 per cent calcium nitrate suppressed the fire to where thermite and thermite starter would not ignite, and wood shavings had to be added. The mixed nitrate calcium carbonate fire was of much less intensity even after ignition by another 20 pounds of thermite. Oxidation of wood is readily possible, however,

and bad fires are possible. At no time did it appear that this fire could not be rapidly extinguished. More white fumes were apparent during the more moderate fire of the 60-40 mixture. A fire truck had no trouble in quickly extinguishing the latter fire after maximum burning rates were observed. The steam developed on this size fire appeared to be no problem.

From this we conclude that FGAN fires are rapid, impossible to manage if the burning surface is not exposed, intense, may lead to the fuming-off of collected liquids, readily oxidize wood, and are, in general, dangerous rapidly expanding fires. Aeroprill AN gives rapid, intense, oxidizing fires of apparently slower rates of involvement of nitrate. The 60-40 ammonium nitrate-calcium carbonate mixtures are only moderate in burning rate and, while oxidizing, do not develop fuming-off liquids. Such fires can be more readily controlled provided burning is not too remote. These experiments are not truly large scale experiments, but the extrapolation to the burning of larger size piles is, at least in part, evident.

V. AN APPROXIMATION TO A LARGE SCALE EXPLOSION

The second important feature of a large scale ship fire is the development of detonation. The theory developed to explain the ship disasters under this contrast has emphasized the importance of pressure in increasing the maximum allowable temperature that liquid nitrate can achieve. In turn, the temperature controls the rate of decomposition, which for hot zone (propellant type) burning alone is rate limited per surface area, but for liquid ammonium nitrate it is limited only by the maximum allowable temperature attained under the prevailing pressure.

The closed and partially vented bomb tests of both Picatinny and the Bureau of Mines have been fully rationalized on the above theory in Progress Report 9.

However, since neither tests were directly applicable to the ship detonations, it would be important to develop a scaled experiment involving several hundred pounds of ammonium nitrate where scaling involved only the non-critical variables which are necessary to the development of a reasonable pressure and temperature and, therefore, rate of reaction and, finally, detonation.

In lieu of the large scale self-heating experiment, we have attempted to carry out in a pipe an experiment which approximates the action within a vertical cylinder in the burning cargo of ammonium nitrate. The requirements are: (1) that the venting is through the nitrate itself, (2) that we provide no confinement except that which could occur on the ship under 20 feet of bagged nitrate, (3) that we provide fire by rapid heating without gas evolution other than from the decomposing nitrate, (4) that we use the largest practical size pipe to give the best possible approximations to the actual conditions within the limits of the size of the charge that can be exploded at the site available for the experiments.

The previous experimentation of the Picatinny Arsenal indicated that 3000 pounds of ammonium nitrate in a bomb ignited by fire would not detonate if a hole of five inches in diameter vented the gases. The Bureau of Mines data indicated that a hole of 3/8 inches in diameter for a five-pound charge did not achieve detonation on the development of a fire in hot nitrate. How the venting area is related to the mass or burning area is unknown and incalculable. Qualitatively, the former experiments require

at least 0.7 square inches of venting per 100 pounds of cold nitrate to prevent explosion, while the latter experiments require at least 2.2 square inches of venting per 100 pounds of heated nitrate to prevent explosion. These two sizes of vent are, of themselves, interesting.

In both of these experiments there was little opportunity for pressure to develop as a result of the pressure drop in the unreacted nitrate created by the escape of large volumes of gases.

As an approximation to these requirements, we have chosen to experiment with a 21.5 foot long 6 inch diameter pipe which holds approximately 170 pounds of ammonium nitrate when fully loaded.

To determine how much ammonium nitrate we could use in an experiment within the demolition area of the testing grounds at the Maynard Back-up Storage Area, we first set off 15 pounds of Hercules FGAN coated with wax "B" under 4 feet of partially damp sand boosted with a 2 1/2 pound demolition block[1] and a No. 12 blasting cap. As observed from 100 yards, practically no sound was heard, and a hole made was about 9 feet in diameter and 3 1/2 feet deep. Second, 85 pounds of the same material was detonated 3 feet below ground with a demolition block; the sound was moderate to strong; the cloud of sand was about 50 yards in diameter and full of brown fumes indicating some incomplete reaction. The hole left was 15 feet in diameter and 5 feet deep. In neither case was there any unreacted nitrate found in the hold.

In an attempt to determine if detonation will propagate in a pipe of this approximate diameter we filled a 5 inch diameter 5.7 feet long cardboard tube with 45 pounds of the above nitrate and in one end used a similar demolition block as before. The

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1. Aluminized R.D.X.

whole tube was buried under about 3 feet of loose sand and set off. The sound was only moderate, with a somewhat smaller cloud which again contained red fumes. The hole was several feet deep and elongated. A few pieces of both cardboard and undetonated but compressed FGAN were found in the last inch of the tube. Aside from this, there was every indication that the detonation had progressed substantially the length of the tube. (Recent data by Prof. A. R. Ubbelohde at the Fourth International Symposium on Combustion and Detonation, Cambridge, Mass., September 1952, indicates the ratio of the depth of the burning zone during detonation to the minimum charge radius that will allow the propagation of detonation is about 0.2. With burning depths of the order of one to two centimeters for the lowest detonation velocity, a diameter of two to four inches is required to allow the propagation of detonation. This diameter is, of course, a function of the confinement, but this estimate gives a measure to guide experimentation.)

The preliminary tests assured that detonation could take place down the length of the tube and that the charge necessary to fill a pipe 21.5 feet long and 6 inches in diameter which was buried under sand was allowable on the range. The pipe was buried except for its ends under 4 feet of earth in the manner shown in the schematic drawing given in Figure 1.

I. The first experiment was filled, in the first six feet from the firing end, with the ignitor; beyond this in the next 10 feet, 100 pounds of Hercules FGAN coated with 0.8 per cent wax "B" was inserted with a piece of paper bagging approximately every 15 to 20 cm. Also included was five pounds of charcoal carbon dispersed in the nitrate. The last five feet was filled with relatively dry sand. This end was not closed, except for two 1/2 inch, pointed expansion bars which were clamped inside the pipe to form a cross.

The ignitor consisted of a 6-foot cardboard tube, 5 inches in diameter in which was laid out 33 thermite ignitors fused by placing 5 grams of thermite starter (31 $\pm$ 0.5 per cent $Ba\,O_2$, 29 $\pm$ 0.5 per cent $Fe_3\,O_4$, and 40 $\pm$ 1 per cent Al) in a cellophane bag within another bag of 28 grams of thermite (Fe_3O_4, Al.) to which was attached one 40-gram charcoal bricket. The starter was fused by 4 inches of 4 seconds per inch fuse from one ignitor to the next in long chains. These starters and 32 pounds of FGAN were placed in the cardboard tube whose ends were closed by 2-inch thick wooden plugs. The tube, in turn, was inserted into the 6-inch pipe, which was closed by a cast iron pipe cap fitted with two spark plugs for the electric contact to three electric squibs which started the first ignitors in the chain.

The pipe was black iron steam pipe; the cap was cast iron made for continuous use at 125 pounds steam pressure or 175 pounds dry gas pressure.

The charge was set off from a considerable distance, and in two minutes brown fumes were seen to come from the open end of the pipe. In five minutes, puffs of FGAN were thrown out of the pipe, and by six minutes the entire contents of the pipe was blasted with considerable velocity out of the pipe by the gas pressure. The bar clamps were bent out of the way, and the charge was scattered substantially 100 feet in front of the pipe with some material to 140 feet from the pipe, making at this distance a span of about fifteen feet.

Eleven of the ignitors had not been started. There was evidence that only three mild fires had been initiated. In spite of this, considerable pressure was developed. It is probable from this that if the nitrate were a free-flowing granular material, the pressure developed by a fire would probably only erupt and scatter quantities of nitrate. In effect, the experiment "discovered" the gun!

II. Several changes were made in the second experiment. Fifteen feet of the pipe was filled with 145 pounds of Hercules FGAN with wax "B" mixed as before with bagging paper. The venting end was partially closed by a pipe cap containing 15 one-half inch and 33 three-quarter inch holes as shown in Figure 1. This gives an area of 62 per cent of the open six-inch pipe but prevents the entire contents from being fired from the tube as a projectile. The venting area is ten square inches per 100 pounds of charge, which is nearly five times the area to weight ratio used in the Bureau of Mines partially vented bombs for heated nitrate. The difference, of course, is that venting must take place through the long column of nitrate.

The ignitor was again assembled outside the pipe in a five-inch cardboard tube. First, wrapping paper was rolled to form a six-foot long, one-half inch inside diameter tube which was filled with 310 g of thermite starter. Two electric squibs were wired to ignite the starter. The tube was placed coaxially in a six-foot 1-1/8 inch rolled paper tube which was filled with 1500 grams of the thermite. This tube was placed coaxially in the cardboard tube containing about 4 kilograms of charcoal brickets broken into at least six pieces, as well as 25 pounds of FGAN. The ends of the tube were closed only by paper (no wooden plugs). The ignitor was inserted into the pipe and the pipe closed as before.

Ten seconds after firing brown fumes emerged from the perforated pipe cap. In 25 seconds, a moderately strong explosion occurred which was easily heard inside a house half a mile distant. A cloud of bright fire and white fumes shot out from the hot end at an angle of about 45°, being deflected by the protective earth works around this end (see Figure 1). The burning materials set fire to about 100 square feet of grass near the end. Brown fumes were not observed.

On approaching the remains, debris was found 30 feet from the ignitor end of the tube, and molten iron (from thermite) was found 20 feet from the end. The split-off flat end of the cast iron pipe cap with the two spark plugs was found 30 feet from the pipe, its energy having been largely dissipated in the protective earthwork. The break in the pipe cap was clean and regular around the edge, and there was no evidence of failure as a result of a casting defect.

The unusual feature of the explosion was that the pipe had moved 14.5 feet out of the pile of earth in spite of the one-inch projecting ring of the broken pipe cap's remaining firmly in place. The tube was hot to the touch to within about 12 feet of the vented end of the pipe, from which place on it was cold. Examination showed the nitrate absent from 11.7 feet of the hot end or about 100 pounds was reacted or blown out, the remainder staying in the tube. The remaining nitrate was free flowing, and there was no collected melt. The pipe remained buried about six to seven feet after the explosion, and it took full power of a five-ton truck to withdraw it from the edge of the pile. This experiment "discovered" the rocket!

Since the pipe cap was rated for 175 pounds per square inch and the safety factor on this dynamic experiment might have allowed a pressure well beyond 400 pounds per square inch, a total force and, therefore, thrust of well over 12,000 pounds must have been operative. These forces are reasonable, considering the motion of the pipe during the explosion. A careful measure of the pipe circumference at both the explosion and cold ends revealed no change as the result of the explosion.

Since a pressure of at least 400 pounds per square inch was developed in only 25 seconds, it is easy to understand the power of an ammonium nitrate explosion from fire. Why detonation did not take place is not clear in view of the Bureau of Mines data giving 300 psi as the pressure for which detonation may occur for FGAN plus 1.5 per cent paper heated to about 150°C.

The explanation appears to lie in two factors: (1) the present sample was at about 25°C, while the Bureau of Mines samples were at about 150°C and (2) the rapid (propellant type) burning developed by the thermite and charcoal did not allow the collection of molten ammonium nitrate which, allowing sufficient time under high pressures, could self-heat to above 400 to 450°C where the very fast rates of decomposition by detonation can take place.

It would appear in the Picatinny large bomb where only 45 seconds was required for detonation that, if sufficient pressure is developed, detonation can take place in cold materials as if set off by a boosting explosive. In the Bureau of Mines experiments, it seems that for FGAN plus 1.5 per cent paper, a recorded temperature of 150° is enough for uniform rapid self-heating to detonation. However, in the presence of a partial vent and a thermocouple lag of many degrees at the time of explosion, self-heating throughout as the result of reaction throughout may be reasonable and initially above 150°C. This interpretation could, due to the rapidity of the changes, be consistent with the Bureau of Mines quenched bomb data as well.

Finally, the lack of detonation in the pipe could be the result of: (1) an improbable event, (2) failure of the detonation to propagate through the paper present, (3) the difficulties in the initiation of detonation in a six-inch radius in the cold nitrate.

VI. CONSIDERATION OF THE GAS PHASE DETONATION THEORY

The theory that the detonation of accumulated unburned gases within the free volume of the cargo vessels which were involved in the ammonium nitrate disasters initiated the detonation of the entire cargo has been considered by several investigators, for example, Picatinny Report Serial No. 1658, July 11, 1947.

To test this proposal by a critical demonstration, experimentation with a hydrogen-oxygen shock tube was employed and was reported in Progress Report 6. While the gas phase detonation theory was clearly rejected on the basis of these experiments, there remained the possibility that initiation by gas phase detonation was an improbable event, hard to observe in but a few experiments, but highly probable in the long duration of a large scale fire.

Two methods could clarify this uncertainty: (1) the performance of a sufficiently large number of these same shock tube experiments to include the event which may be improbable, or (2) the development of a qualitatively more severe shock than any gas phase reaction can produce and thus to achieve a condition of high probability in which to test the validity of the theory.

The shock developed in a stoichiometric mixture of hydrogen and oxygen is more intense than the shocks produced by the detonation of any of the partially oxidized products of ammonium nitrate decomposition even in the presence of charcoal, wax, paper, etc. However, the shock produced by a confined explosion of a blasting cap can be made many times more intense than the hydrogen-oxygen shock. Consequently, a series of five experiments were performed to test critically the gas phase

detonation theory at a level of shock intensity to produce a highly probable detonation of the ammonium nitrate, if such a detonation is possible by this mode of initiation.

(1) A No. 6 blasting cap was buried in about 15 pounds of wax-coated FGAN at ambient temperature and fired. The nitrate was scattered, but there was no detonation and no evidence of any burning.

(2) A No. 6 blasting cap was mounted in a three-quarter inch diameter by six inches long iron pipe capped on one end. This shock tube was mounted above a one-quart wide mouth Dewar (in which molten ammonium nitrate was vigorously decomposing under the effects of $K_2Cr_2O_7$ catalyst) and could be lowered on the burning of a short distance of fuse. About two pounds of CPAN at 240 - 250°C was placed in the Dewar under the shock tube; the dichromate was added, and the nitrate rapidly fumed off, prior to the burning of the fuse link, leaving only a small sample of ammonium nitrate liquid and foam. The firing of the blasting cap produced no tangible effect.

(3) The experimental setup was modified to lower the exposed No. 6 blasting cap into the Dewar remotely. About two pounds of CPAN, heated to 250°C, were catalyzed by $K_2Cr_2O_7$, and at the maximum of the reaction a weighted blasting cap was lowered well into the liquid below the surface and fired. The liquid detonated, producing an easily recognized air shock and an intense sound which alerted personnel more than one-half mile distant and brought them to investigate. The cast iron apparatus for supporting the sample was broken cleanly into several pieces.

(4) The same size charge was again used, and the blasting cap was again placed in the six-inch by three-quarter inch shock tube. This sample was not heated to much above 180°C and did not

self-heat by the addition of $K_2Cr_2O_7$. The firing of the cap onto a sample whose surface was cooling and forming a solid film of ammonium nitrate did not detonate or modify the sample or produce local burning.

5. The last experiment was repeated with heated, catalyzed CPAN, and the shock tube was lowered well into the foaming liquid nitrate. The blasting cap was separated by an air gap or four to five inches, but the mouth of the shock tube was well placed in the liquid. The cap was fired at the maximum of the foaming process. There was no observable effect, except the breaking of the Dewar and the spilling of the liquid.

Conclusion: Since the blasting cap in a pipe nipple produces a high intensity shock wave, since this shock was transferred to the foaming nitrate by a short air gap without the detonation of the liquid, since a blasting cap in the hot catalyzed liquid causes detonation of the liquid, and since the cap does not set off the solid, we conclude that the conditions for shock initiation were very much more favorable to the development of detonation than in the previous experiments and in the gas phase detonation in the free spaces of the cargo vessel above a burning cargo of ammonium nitrate. Therefore, the gas phase detonation theory of the ammonium nitrate initiation is believed to be without substantiation, in fact, and is categorically rejected as a cause of the disasters of the "Grand Camp," "High Flyer," or "Ocean Liberty."

SCHEMATIC DIAGRAM OF THE BURIED PIPE EXPERIMENT

Figure 1

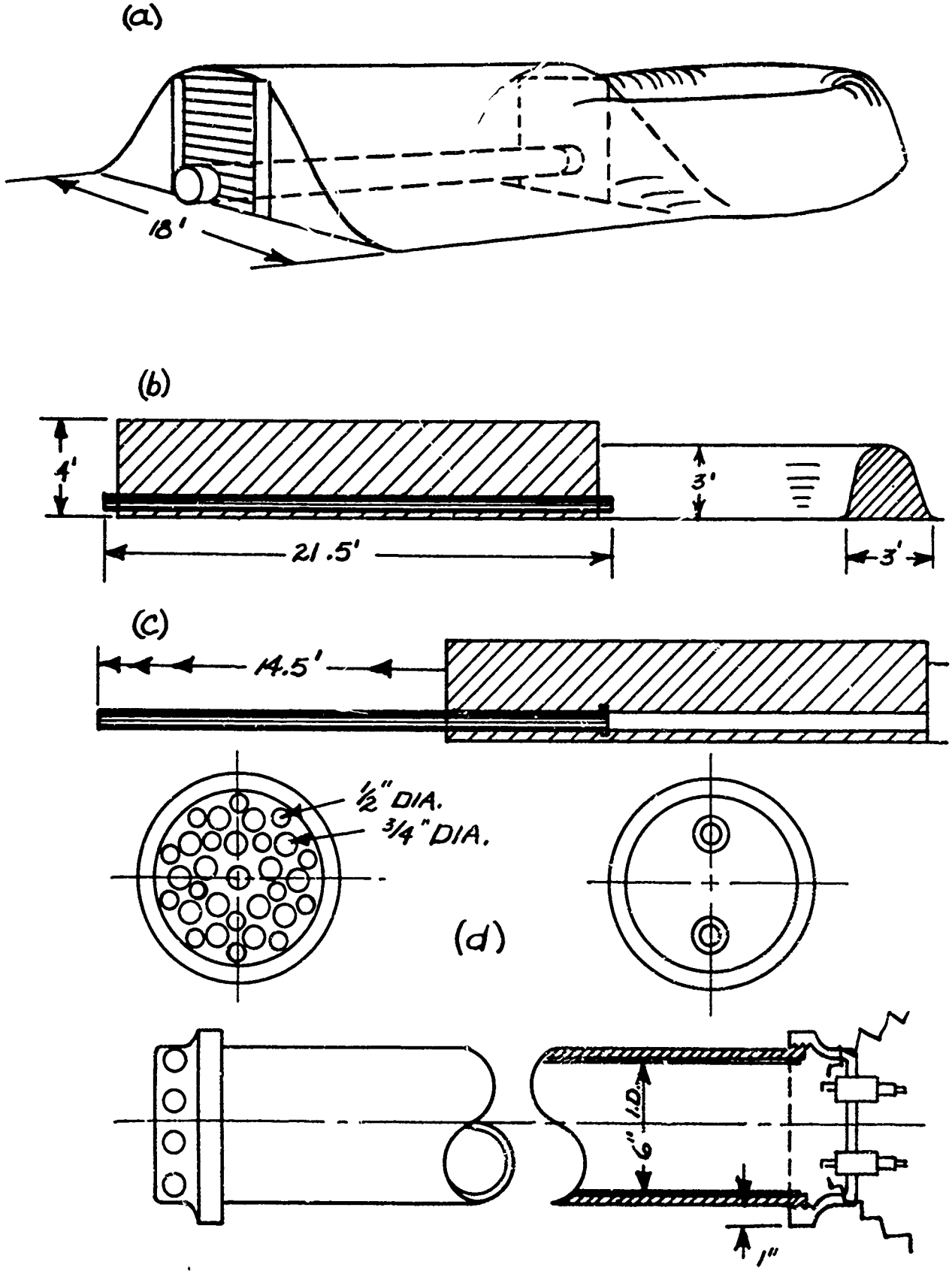
(a) General Form of the pipe and barricade

(b) Cross section prior to firing

(c) A cross section showing displacement of pipe after second experiment

(d) Sectional views of the pipe before the second experiment broken line shows the position of cap fracture resulting from the second explosion

FIGURE 1



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APPENDIX I

p.283

Information Concerning Ammonium Nitrate,
Ammonium Sulfate Double and Mixed Salts

A. Translated from: "Gmelin's Handbuch ser Anorganischen Chemie 23 Ammonia, Pages 283-288.

The System $(NH_4)_2SO_4$ - NH_4NO_3.

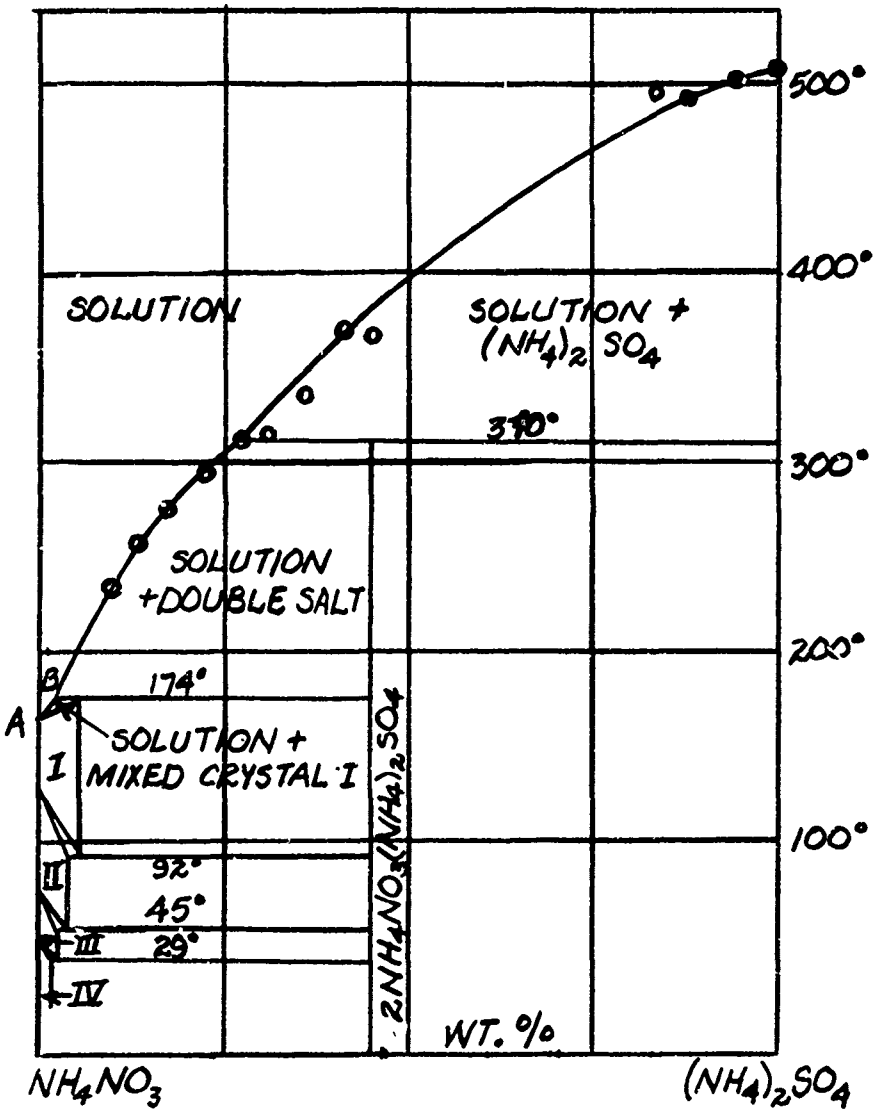
Melting points of $(NH_4)_2SO_4$ and NH_4NO_3 mixtures; composition in weight - percent $(NH_4)_2SO_4$:

$(NH_4)_2SO_4$	M. P., °C.
0.17	169.9
0.39	170.3
0.92	171.5
1.5	172.5
2.1	173.6
3.04	175.7
4.6	177.7
5.6	178.6
8.2	180.6
9.5	180.5
11.6	180.8
13.9	180.8

The steady increase in melting point upon addition of $(NH_4)_2SO_4$ indicates that NH_4NO_3 and $(NH_4)_2SO_4$ solid solutions are the only solid phase. No eutectic is formed, according to E. P. Perman and W. J. Howells, J. Chem. Soc. 123, 2129 (1923). According to F. A. Freeth, J. Phys. Chem. 29, 506 (1925), the composition of

the eutectic is immediately adjacent to the composition of the compound NH_4NO_3, and the rising curve is the liquid curve of the double salt $(NH_4)_2SO_4 \cdot 3NH_4NO_3$. However, in agreement with the concepts of E. P. Perman and W. J. Howells (l.c.), when a mixture containing 4 percent $(NH_4)_2SO_4$ is examined under a heated-stage microscope, cooling of the fused mass is observed to be accompanied by the formation of only a single, homogeneous, isotropic solid-solution phase, which is transformed only at about 100°C into an inhomogeneous birefringent mass containing a recognizable quantity of the tetragonal modification of NH_4NO_3. Upon reheating, the mass becomes isotropic again at only 118.5°C. According to N. L. Bowen, J. Phys. Chem. 30, 736 (1926), the solid solution extends at least as far as 4 weight - percent, but probably beyond 8 weight - percent, of $(NH_4)_2SO_4$. Figure 29 shows the phase diagram according to E. Janecke, W. Eissner, and R. Brill, Z. Anorg. Chem. 160, 174 (1927), including the solid-solution areas with the NH_4NO_3 modifications I, II, III, IV. All transformation temperatures of NH_4NO_3 are shown to be considerably reduced. However, according to N. L. Bowen (l.c., Page 737), presumably neither the tetragonal nor the orthorhombic form of NH_4NO_3 takes up any sulfate into solid solution. The experiments were carried out in a sealed tube above about 200°C. Since, on the basis of investigations in the system NH_4NO_3; $(NH_4)_2SO_4$, H_2O, the existence of the double salt $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ is doubtful, there begins above 174°C the liquid curve of the compound $(NH_4)_2SO_4 \cdot 2NH_4NO_3$, which melts incongruently at 310°C (E. Janecke, W. Eissner and R. Brill, l.c., page 73). Concerning the thermal decomposition of $(NH_4)_2SO_4$ - NH_4NO_3 mixtures at higher temperatures, cf. Page 287.

GMELIN - NH_4 P. 283 FIG. 29



THE SYSTEM

↑ 62.3%

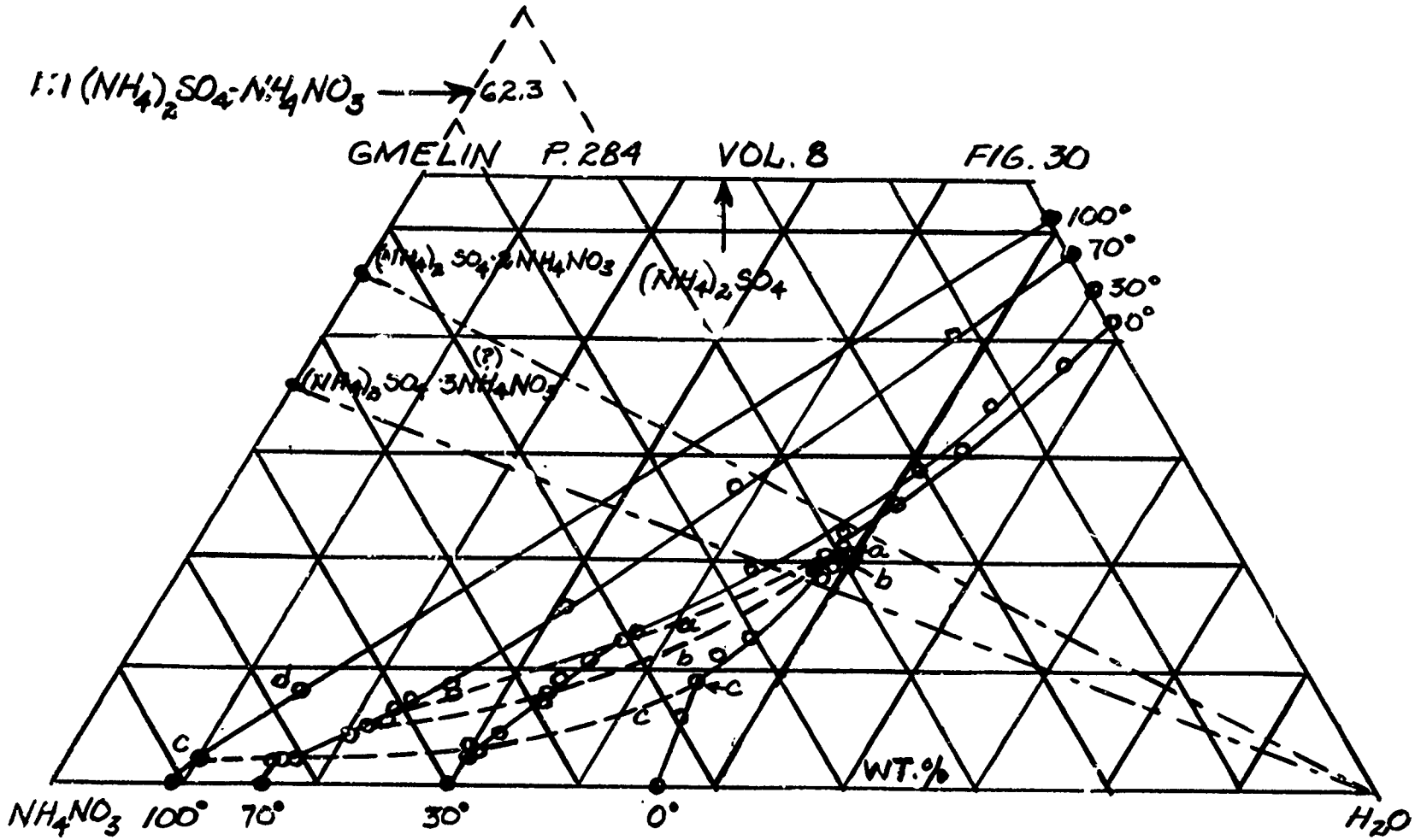
1:1 NH_4NO_3 $(NH_4)_2SO_4$

The System $(NH_4)_2SO_4$; NH_4NO_3; H_2O

The following solids appear between 0°C and 100°C: $(NH_4)_2SO_4$, $(NH_4)_2SO_4 \cdot 2NH_4NO_3$, $(NH_4)_2SO_4 \cdot 3NH_4NO_3$(?), NH_4NO_3. Concerning experiments on the separation of $(NH_4)_2SO_4$-NH_4NO_3 mixtures or compounds in the molecular ratios 1:3 and 1:2 on the basis of investigations of the system, cf. W. Gluud, W. Klempt, and F. Brodkorb, Ber. Ges. Kohlentechn, 3, 170 (1929/1931)

Solubility. Figure 30 shows the isotherms at 0°, 30°, 70°, and 100°C, based on investigations by F. A. H. Schreinemakers and P. H. J. Hoenen, Chem. Weekbl., 6, 52 (1909) at 30°C, by A. J. C. de Waal, Dissert. Leyden 1910, 78 at 0°C and 70°C, and by E. Jänecke, W. Eissner and R. Brill, Z. Anorg. Chem. 160, 172 (1927) at 0°C, 30°, 70°, and 100°C. The polytherms of solutions saturated with two solids are drawn as broken curves, (a) giving the composition of solutions saturated with $(NH_4)_2SO_4$ and $(NH_4)_2SO_4 \cdot 2NH_4NO_3$, (b) of solutions saturated with $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ and $(NH_4)_2SO_4 \cdot 3NH_4NO_3$(?), and finally (c) of solutions saturated with $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ (?) and NH_4NO_3. According to E. Jänecke, W. Eissner and R. Brill (l.c.), the solution in Point (d) of the 100°C isotherm is saturated with double salt and $(NH_4)_2SO_4$. Also plotted in Figure 30 is the chyohydrate $(NH_4)_2SO_4$ -NH_4NO_3-ice, which, according to D. Mazzotto, N. Cim. (3) 29, 25 (1891), lies at -21.0°C, 22.6 weight-percent $(NH_4)_2SO_4$, and 21.0 weight - percent NH_4NO_3 (recalculated).

The incongruent solubility of the double salts is apparent from the diagram. The double salt $(NH_4)_2SO_4 \cdot 3NH_4NO_3$ (?), however, should be recrystallizable from water, without decomposition, at 0°C. Nevertheless, according to microscopic studies by E. Jänecke, W. Eissner and R. Brill, Z. Anorg. Chem. 160, 173 (1927), such a solid does not



THE SYSTEM $(NH_4)_2SO_4$-NH_4NO_3-H_2O

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exist; the illusion of its existence is caused by the formation of a crust of $(NH_4)_2SO_4.2NH_4NO_3$ on NH_4NO_3. Concerning the continuation of the solubility diagram as far as anhydrous mixtures and the occurence of solid solutions, cf. E. Jänecke, W. Eissner, and R. Brill (l.c.)

Vapor Pressure of solution saturated with NH_4NO_3 and $(NH_4)_2SO_4$ at 30°C: 19.82 mm Hg, according to J. R. Adams and A. R. Merz, Ind. Eng. Chem. 21, 306 (1929).

$(NH_4)_2SO_4.2NH_4NO_3$.

Occurs as a solid phase in the systems $(NH_4)_2SO_4$-NH_4NO_3 and $(NH_4)_2SO_4$-NH_4NO_3 - H_2O; for details, cf. Page 283. Precipitates from a solution of the components saturated at room temperature and containing an excess of NH_4NO_3, in the course of 6-10 weeks, in plate-like crystals a few centimeters in size, which consist almost exclusively of twin formations (E. Jänecke, W. Eissner and R. Brill, Z. Anorg. Chem. 160, 175 (1927)). Contrary to the data of R. Robertson, Trans. Faraday Soc. 20, 50, (1924/1925), and of H. H. Thomas and A. F. Hallimond, Trans. Faraday Soc. 20, 55 (1924/1925), in accordance with which the double salt, depending upon its origin or preparation from a cold or hot solution, below or above 30°C, is supposed to exhibit the habit of either NH_4NO_3 or $(NH_4)_2SO_4$, coupled with correspondingly different optical properties, E. Jänecke, W. Eissner, and R. Brill (l.c., Page 178) were unable to recognize a habit comparable to that of the components either in comparatively large crystals prepared in the laboratory or in technical products. Orthorhombic pyramidal crystal class. Axial ratio a:b:c = 1.106:1:3.804. Lengths of edges of unit cell: a = 11.22 Å b = 10.18 Å, c = 38.5 Å; $\alpha=\beta=\gamma=90°$. 16 molecules in the unit cell. The crystal molecule

consists of at least $2((NH_4)_2SO_4.2NH_4NO_3)$, according to E. Jänecke, W. Eissner and R. Brill (l.c. Pages 177, 179, 182, 184). In contrast with this, X-ray investigation of crystals of varying external habits, obtained from cold and hot solutions, and of technical salt from Oppau shows, according to W. Bragg, Trans. Faraday, Soc. 20, 59, 60 (1924/1925), consistent indications that the substance belongs to the triclinic (probably pedial) crystal class, completely different for the unit cell from the data given above: a = 4.92 Å, b = 5.88 Å, c = 10.28 Å; α = 92° 57', β = 82° 11', γ = probably close to 90°. One molecule in the unit cell. According to R. Robertson (l.c. Page 51), measurements of the density $L^{15.5}_{15.5}$ of crystals obtained from hot and cold solutions give values between 1.672 and 1.678, of technical salt 1.671 to 1.683, of a mixture of 1 mol $(NH_4)_2SO_4$ and 2 mols NH_4NO_3 1.738. Incongruent melting point 310°C, indices of refraction for Na light: n_α = 1.519, n_β = 1.528, n_γ=1.534; birefringence negative, according to E. Jänecke, W. Eissner and R. Brill (l.c. Pages 175, 178). Indices of refraction for crystals obtained from cold solution and showing the nitrate habit: n_α = 1.469, n_β = 1.528, n_γ = 1.543; birefringence negative, indices of refraction for crystals showing the sulfate habit: N_α = 1.521, n_β = 1.531, n_γ = 1.536, according to H. H. Thomas and A. F. Hallimond (l. c., Pages 56, 57).

In contrast with NH_4NO_3, $(NH_4)_2SO_4$. 2 NH_4NO_3 is very stable in moist air; according to F. Brodkorb, Ber. Ges. Kohlentechn, 3 171 (1929/1931), it does not cake or form lumps; cf. also the data on the behavior of technical ammonium sulfate in the air, as well as on its behavior upon heating, in the section entitled "Thermal Decomposition, Explosive Decomposition", Pages 286, 287.

It is decomposed by water with separation of $(NH_4)_2SO_4$; it is stable only in contact with solutions containing an excess of NH_4NO_3, according to F. A. H. Schreinemakers, and P.H.J. Hoenen, Chem. Weekbl. 6, 51 (1909); cf. Figure 30, Page 284.

$(NH_4)_2SO_4 . 3NH_4NO_3$ (?)

Is supposed to occur as a solid in the system $(NH_4)_2SO_4$-NH_4NO_3, as well as, on the basis of investigations carried out by the residue method by F. A. H. Schreinemakers and P. H. J. Hoenen, Chem. Weekbl. 6, 51 (1909), and by A. J. C. de Waal, Dissert. Leyden 1910, 78, 80, in the system $(NH_4)_2SO_4$; NH_4NO_3; H_2O; cf. Page Page 283. On the other hand, E. Jänecke, W. Eissner, and R. Brill, Z. Anorg. Chem. 160, 171, 173 (1927), have shown by microscopic examination that the solid possessing the composition $(NH_4)_2SO_4 . 3NH_4NO_3$ is not homogeneous, the illusion of a compound being created by a crust of $(NH_4)_2SO_4 . 2NH_4NO_3$ over NH_4NO_3. Verification by the residue method also confirms the non-existence of the compound $(NH_4)_2SO_4 . 3NH_4NO_3$. Density $D_{15.5}^{15.5} = 1.675$, according to R. Robertson, Trans. Faraday Soc. 20, 51 (1924/1925). Indices of refraction for Na light: $n_\alpha = 1.221$*, $n_\beta = 1.533$, $n_\gamma = 1.536$; birefringence negative according to H. H. Thomas and A. F. Hallimond, Trans. Faraday Soc. 20, 57 (1924/1925).

Technical Ammonium Sulfatesaltpeter

Leuna Saltpeter, Oppau Salt

Technical ammonium sulfatesaltpeter of normal composition contains 50 weight percent each of $(NH_4)_2SO_4$ and NH_4NO_3, and therefore approximates the composition of the double salt $(NH_4)_2SO_4 . 2NH_4NO_3$ (see p. 285) which has 45.2 wt percent $(NH_4)_2SO_4$ and 54.8 wt. percent of NH_5NO_3, but has a slight excess of $(NH_4)_2SO_4$. In the

*Apparently a typographical error; should probably be 1.521.

following investigation not only normal sulfate saltpeter was studied but also products with excess NH_4NO_3. These substances probably consist in most cases of a mixture of the double salt and the component present in excess. On the question "near which regions microcrystalline formation will take place?" see "The System NH_4NO_3 - $(NH_4)_2SO_4$" on p. 283. In the following section data will be given on the chemical behavior of the technical product in air and on heating. For the technical preparation see the descriptions of the individual ammonium compounds in the final chapter.

Hygroscopicity, Caking and Deliquescence

See also the behavior of ammonium nitrate in air on p. 107 (not in this translation). The statement that ammoniumsulfat-saltpeter (leunasaltpeter) is less hygroscopic than NH_4NO_3 is only true to a limited extent. The difference increases with rising temperatures and decreasing atmospheric moisture. At 10°C and a relative humidity of 100 percent the difference is slight. At 20° and 75 percent the lower hygroscopicity of the mixed salt is clearly evident. The rate of water absorption is constant at a given temperature and humidity, therefore the moisture already present in the salt is unimportant; likewise its grain size and whether the product is obtained by mechanical mixing or simultaneous crystallization of its components. The ratio of sulfate to nitrate in the mixture has little influence. On the other hand the rate is inversely proportional to the thickness of the layer. The absorption takes place chiefly in the outer layer of the salt, from which a saturated solution diffuses into the inner portion. Covering the salt with sand or gypsum greatly reduces it. G. I. Goratein (J. Chem. Ind. (USSR) 10, number 7 (1933) 47; C 1934 I 2475).

For a comparison of the decrease in hygroscopicity of NH_4NO_3 by mixture with $(NH_4)_2SO_4$ see further S Wolfkowitsch, R. Remen (USSR Naučno-Tech. Upravlenie V. S. N. Ch. (Russ) Nr 216 (1927); C. 1929 I 1498) - The water content of ammoniumsulfatsaltpeter (ratio of nitrate to sulfate in the mixture not given) which had been dried at 130°C and then spread out in layers of 5 - 7 mm thickness and stored for 7 days in air at 20.1°C and the following relative humidities, is

Air relative humidity	97.5	87 75	78.0	73.0	68.0
Water content percent	36.2±0.2	25.9±0.1	11.±0.1	7.2±0.1	2.6±0.2

At humidities above 87.75 percent the salt begins to deliquesce, A. B. Beaumont, R. A. Mooney (Ind. Eng. Chem. 17, (1925) 635).

The decrease in agglomeration was estimated by A. B. Beaumont and R. A. Mooney (loc. cit.) by measuring the compressive strength of a salt which had been dried at 130°C, then stored for 14 days at 20.1°C and at relative humidities from 97.5 percent to 78.0 percent and then dried in a mold. - Compared with NH_4NO_3, the tendency to agglomeration of ammoniumsulfatsaltpeter (Leunasaltpeter) between 20°C and 40°C is substantially less. On storing of compressed material (pressed under a pressure of 55 atmos.) at 20°C. and constant humidity, the solidity increases but little with low water content salt (about 0.5 percent); but with higher water contents (3 - 5 percent) on the contrary it became great inside of 24 hours, probably due to the bonding together with the formation of the double salt $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ (the so-called maturing). In the matured form the increase in solidity on storage is less and is independent of the water content, G. I . Gorstein (loc. cit). Under pressure (1.13 kg/cm^2 excess pressure) wholly dry ammoniumsulfatsaltpeter (Oppau) salt alone will not cake together after previous heating.

On the contrary caking together will take place in the salt in presence of moisture since the saturated solution crystallizes out in the spaces between the salt grams. R. Robertson. (Trans. Faraday Soc. 20, 53-54 (1924-25).

Thermal Decomposition, Explosive Decomposition

A great explosion catastrophe occurred in 4,500 tons (metric) of ammoniumsulfatsaltpeter in a loaded bin in the ammonia and synthetic fertilizer factory of the Badische Anilin and Soda Works at Oppau (it is estimated that only about one tenth part of it actually exploded) on Sept. 21, 1921 at 7:32 A.M. The number killed (586) and injured (1952) caused a series of publications concerned with this accident and its probable causes to be written for example (anonym in Ch. Ztg. 45 (1921) 937), E. Hene (Ch. Ztg. 45 (1921) 965, 1085), G. Rosendahl (Ch. Ztg. 45 (1921) 1034), P. Wachtel (Ch. Ztg. 45 (1921) 1188), anonym in Z. ang. Ch. 34 (1921) 489), A. Stettbacher (Schweiz, Ch. Ztg. 1921, 512), E. Lefevre (Ind. chim. 8 (1921) 390), (anonym in Rev. Prod. chim. 1921, 589), C. Commentz (Chem. met. Eng. 25 (1921) 818), J. Kendall (Chem. met. Eng. 25 (1921) 949), (anonym in Chem. Trade J. 69 (1921) 458), (anonym in J. Soc. Chem. Ind. Rev. 40 (1921) 381), Chabanier (Monit. scient. (5) 11 (1921) 225), Badische Anilin- and Sodafabrik (Ch. Ind. 45 (1922) 46), Fleischmann (Z. ang. Ch. 35 (1922) 96), G. A. Brender A. Brandis (Het Gas 42 (1922) 12), L. Wohler (Z. ang. Ch. 37 (1924) 497), R. Escales (Z. gesamte Schiess- und Sprengstoffwesen 19 (1924) 44, 60), Baumann, Bertram, Kempf, Kuhn, Schreiber (Z. gesamte Schiess-und Sprengstoffwesen 19 (1924) 71, 90) See also the literature review assembled by H. Kast (Z. gesamte Schiess-und Sprengstoffwesen 20 (1925) Nr. 11, special number S2, note 2).

The most comprehensive investigations were carried out by H. Kast of the Chemisch-Technische Reichsanstalt in Berlin, von H. Kast (Z. gesamte Schiess- und Sprengstoffwesen 20 (1925) Nr. 11, 12, Sonder-Beilage, 21 (1926) Nr. 1 bis 9, Sonder-Beilage, einige Angaben s. auch Z. gesamte Schiess- and Sprengstoffwesen 22 (1927) 31) sowie durch Chemistry Research Board of the Department of Scientific and Industrial Research, London-Woolwich, von R. Robertson, H. H. Thomas, A. F. Hallimond, W. Bragg and besonders G. Rotter (Trans. Faraday Soc. 20 (1924/1925) 46). In the following citations will simply be made by the numbers used by H. Kast in his literature review referred to above.

Refer also to the sections "Behavior on Heating," and "Explosive Decomposition, Detonation under Ammonium nitrate, page 107, especially p. 110 (not in this translation).

On heating in vacuo at 100° - 120°C. there is a noticeable quantity of gas given off. With the substances NH_4Cl, NaCl, Na_2SO_4 and $NaNO_3$ the gas evolution is very small but with $NaNO_2$, H_2SO_4 and cane sugar it is considerably accelerated, G. Rotter (loc. cit P. 62, 65). In a heating experiment with a Wood's metal bath at 280° it gives white vapors, and a vigorous effervescence. Even at 360° detonation did not take place. Over a free flame ammoniumsulfatsaltpeter decomposed with a violent evolution of gases, which at times ignited and burned explosively. In an iron crucible at red heat it ignited in places, but the flame at once goes out again, and then follows a gassing first with the evolution of NH_3 and later of acid vapors. In a sheet iron container in a wood fire the salt melts and vaporizes without further action, H. Kast (Nr. 1, p. 9). In a glowing porcelain crucible it burns quietly like

NH_4NO_3; N. S. Torsujew (J. Chem. Ind. U.S.S.R. 13, 104 (1936)). On intensive local heating of the salt by means of a mixture of Mg and $KClO_3$ in a steel tube or by Thermite in a steel shell, a relatively slow increase in pressure takes place. Apparently only the nitrate decomposes. G. Rotter (loc. cit, p. 72, 73).

Friction and impact

Friction has no effect on the salt according to H. Kast (No. 2, p. 16. see also Z. gesamte Scheiss und Sprengstoffwesen 22 (1927) 33). According to Rotter (loc. cit. p. 62) in the presence of an abrasive, like emery, a slight decomposition takes place. On impact (drop hammer from 2 to 20 kg in weight), a preparation composed of equal weights of $(NH_4)_2SO_4$ and NH_4NO_3 suffers no change; with a higher nitrate content, a heavy hammer and a high drop a decomposition sometimes takes place either with or without detonation. H. Kast (No. 2, p. 16). G. Rotter (loc cit) caused very slight decomposition under the drop hammer.

With a detonator in a confined space. A small quantity of the salt (ordinarily 10 g total of a mixture of equal weights of $(NH_4)_2SO_4$ and NH_4NO_3) were placed in a Trauzl lead block with a 2 gm. detonating cap but did not explode; H. Kast (No. 1, p. 9; No. 5, p.27). G. Rotter obtained a similar result (loc. cit. p. 66). Experiments with larger amounts of the salt (about 100-300 g. or 1.6 to 2.8 kg) in a wrought iron tube and having (various lengths and diameters but a wall thickness usually of 4 mm) a large detonator (25-370 g. picric acid between the detonator and the salt) there was no immediate extinction of the explosion, but in comparison with NH_4NO_3 there was only a limited spreading of the explosion; H. Kast (No. 1, p. 9, 10; No. 5 p. 27). See also G. Rotter's experiments in steel shells, wrought iron and steel tubes (loc. cit. p. 68). Raising the NH_4NO_3

content raises the explosive property considerably. Even with a product containing 60 wt. percent NH_4NO_4 and with a heavy detonator (100 g. picric acid and a 2 g detonator) and tightly confined, a complete exposing decomposition can be obtained; H. Kast (No. 5, p. 27, see also No. 6 p. 30 and 31). Increasing the grain size of the $(NH_4)_2SO_4$, over that of the NH_4NO_3 in the salt mixture also acts to increase the explosive property; H. Kast (No. 7, p. 35). The transfer heat of decomposition from the nitrate to the sulfate depends on the relative surfaces of the two salts.

The same effect of heat transfer on the explosive properties is obtained by making the sulfate grains coarser or the nitrate finer, Ph. Naoum, R. Aufschläger (Z. gesamte Schiess - und Sprengstoffwesen 19, 36, 37 (1924). An increase in the cubic density causes a rapid decrease in explosive properties. By strongly confining or by the use of a detonator this effect can be balanced. For example a salt mixture containing 65 percent NH_4NO_3 and having a cubic density of 1.2 can only be caused to explode completely when strongly confined (in a 10 cm steel shell). In a container of cardboard cylinder of 3 mm wall thickness and 10 cm diameter, the explosion almost always fails to propagate. Also at a cubic density of 1.0. On very loose packing (loading density 0.75) the normal salt, with 50 wt percent NH_4NO_3, can be caused to go to gas explosively in a strong iron container; evidently because of the favorable swirling up of the loose salt by the pressure wave before the explosion, H. Kast (No. 7, p. 36; No. 8, p. 37; No. 3, p. 18). Generally the salt can be caused to explode only by a powerful detonator. Black powder for example, (100 g. to 2.3 kg salt in a strong wide iron container) is ineffective. Picric acid and Perastralite have

about equal effect when about 2.7 kg of salt mixture with 60 wt. percent NH_4NO_3 are loaded into a wrought iron tube (4 mm wall thickness, 37 cm long, 10 cm diameter); 80 g picric acid or perastralite are about the lower limit of detonator for a satisfactory explosion; H. Kast (No. 8 p. 38, 39). The explosion propagates more easily in a heated mixture. Moisture acts similarly to an inert substance or to increasing the loading density, in hindering an explosion. H. Kast (No. 9, p. 41). Data on the depth and diameter of the crater in frozen ground caused by the explosion of mixed ammoniumsulfatsaltpeter and ammonia given by N. S. Torssujew (J. Chem. Ind. (USSR) 13, 103 (1936) (in Russian); C. 1936 II, 159).

Technical explosive data: Data calculated for the explosion of various salt mixtures whose composition in weight percent $(NH_4)_2SO_4$ and molal ratio $(NH_4)_2SO_4$: NH_4NO_3 are given in the following table. The cubic density in all cases is 1.1.

Wt. percent $(NH_4)_2SO_4$	62.5	56.9	52.4	48.5*	45.2**	29	10
Molar Ratio	1:1	4:5	2:3	4:7	1:2**	1:4	1:15
Heat of Explosion in K Cal/kg	-54	+41	132	195	256	290	330
Explosion temperature	-	180°	470°	720°	1020°	1080°	1190°
Specific gas volume liters per kg	950	940	930	930	920	940	965
Specific energy in Kg/l.	-	1600	2600	3485	4530	4800	5330

* Oppau salt

** Double salt $(NH_4)_2SO_4.2NH_4NO_3$

H. Kast (No. 2 p. 14, see also No. 1, p. 12

The velocity of explosion measured for cubic densities of 0.8 to 0.9 for a mixture with 70 wt percent NH_4NO_3: 2600 to 2900 meters per second; for a salt containing 60 wt percent NH_4NO_3 1900 to 2400 meters per second; for the double salt with 58.4 wt percent NH_4NO_3 about 2000 m/sec.; H. Kast No. 1, p. 12; No. 8, p. 40; see also data in Z. gesamte Schiess - und Sprengstoffwesen 22, 32 (1927).

Translated from the German of "Gmelin's Handbuch anorganische Chemie System nummer 23 - Ammonium" by A. Bozrow and W. J. Murray, June 17, 1952
Arthur D. Little, Inc.

B. Quotation from: J. N. Pring Translation
Faraday Soc. 20 78 ff (1925-1925)

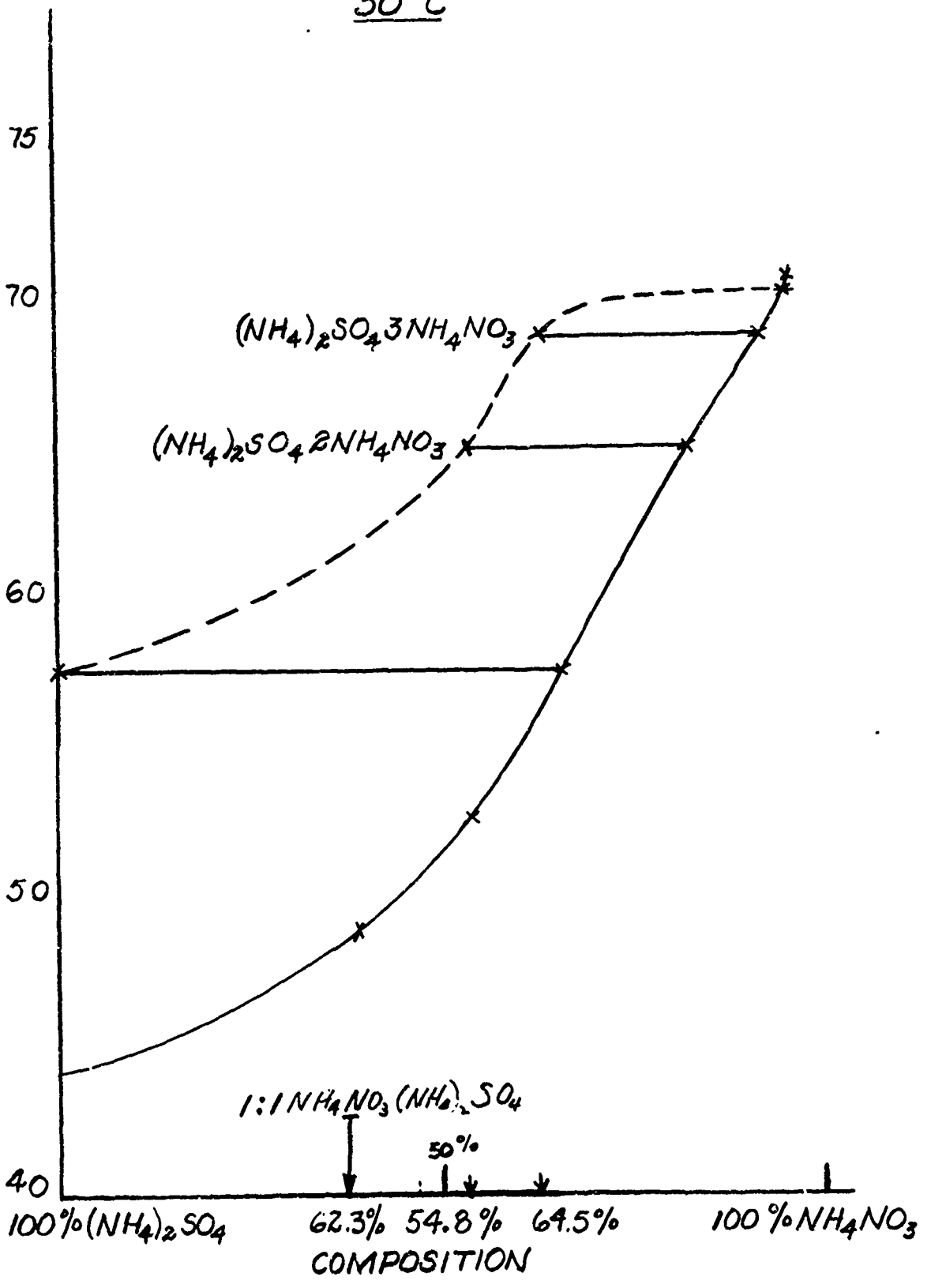
The following quotation is taken from the British investigation of the Oppau disaster as published in the Transactions of the Faraday Society. This quotation documents the statement on Page 16 of Progress Report No. 10 concerning the solubility of Oppau salt in various compositions of ammonium sulfate and ammonium nitrate.

"The relations apply at the constant temperature of 30°C. The continuous curve represents the composition of saturated solutions with the solubility of mixed salts as ordinates and the ratio of ammonium nitrate to ammonium sulphate as abscissae. The dotted curve represents the composition of the solid phase which separates out from the saturated solution of the composition indicated by that point on the continuous curve which is on the same horizontal line. For instance, on evaporating a solution at a constant temperature of 30°C., the salts $(NH_4)_2SO_4$, $2NH_4NO_3$ and $(NH_4)_2SO_4$, $3NH_4NO_2$ containing 54.8 percent and 64.5 percent ammonium nitrate are separated respectively from solutions of the mixed salts containing 82 percent and 94 percent ammonium nitrate. Further, on evaporating at this temperature a solution of a mixture corresponding to $(NH_4)_2SO_4$, $2NH_4NO_3$, only ammonium sulphate is separated. On evaporating a solution of any mixture of the salts, the solid which separates is poorer in ammonium nitrate than the mother liquor which thus becomes progressively richer in ammonium nitrate until a percentage of 96 is reached when the solid phase will have the same composition as the salt in solution. It further follows that if a large amount of the mixed salt $(NH_4)_2SO_4$; $2NH_4NO_3$ is leached with water and an

equilibrium allowed to be attained at 30°C., the solution will contain 82 percent NH_4NO_3. If this is then completely evaporated and the solid again leached, the equilibrium value of the solution will be about 96 percent NH_4NO_3. According to these data, the conditions for segregation are thus clearly seen to be present. In practise, the segregation might arise either during evaporation or subsequently by water, such as rain, percolating through the mass and subsequently drying.

It would appear very desirable to have determined more points on the dotted curve. The data so far consulted offers no evidence for the existence of definite compounds between the salts but merely shows that these complexes are only stable in presence of a large excess of ammonium nitrate. It is submitted that the range of existence of these compounds would be determined by measurements of the change in relative solubilities and the composition of the solid phase at different temperatures in a manner similar, for instance, to that recently worked out in the case of sodium ammonium sulphate by S. M. Levi. "

30° C


SOLUBILITY. GRM PER 100 GRM SATURATED SOLUTION
75
70
60
50
40
$(NH_4)_2SO_4 3NH_4NO_3$
$(NH_4)_2SO_4 2NH_4NO_3$
1:1 NH_4NO_3 $(NH_4)_2SO_4$
50%
100% $(NH_4)_2SO_4$
62.3%
54.8%
64.5%
100% NH_4NO_3
COMPOSITION